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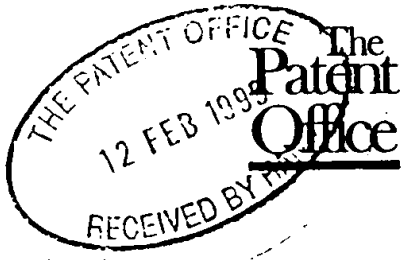

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2. Patent application number *(The Patent Office will fill in this part)* — 12 FEB 1999 — **9903251.8**

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CAMBRIDGE DISPLAY TECHNOLOGY LTD
181A HUNTINGDON ROAD
CAMBRIDGE
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UNITED KINGDOM

Patents ADP number *(if you know it)* — 6166444002

If the applicant is a corporate body, give the country/state of its incorporation — **UNITED KINGDOM**

4. Title of the invention — **OPTO-ELECTRIC DEVICES**

5. Name of your agent *(if you have one)*
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89379

OPTO-ELECTRICAL DEVICES

This invention relates to opto-electrical devices, for example devices for emitting or detecting light.

One specific class of opto-electrical devices is those that use an organic material for light emission or detection. Light-emissive organic materials are described in PCT/WO90/13148 and US 4,539,507, the contents of both of which are incorporated herein by reference. The basic structure of these devices is a light-emissive organic layer, for instance a film of a poly(p-phenylenevinylene ("PPV"), sandwiched between two electrodes. One of the electrodes (the cathode) injects negative charge carriers (electrons) and the other electrode (the anode) injects positive charge carriers (holes). The electrons and holes combine in the organic layer generating photons. In PCT/WO90/13148 the organic light-emissive material is a polymer. In US 4,539,507 the organic light-emissive material is of the class known as small molecule materials, such as (8-hydroxyquinoline)aluminium ("Alq3"). In a practical device one of the electrodes is typically transparent, to allow the photons to escape the device.

Figure 1 shows a typical cross-sectional structure of such an organic light-emissive device ("OLED"). The OLED is typically fabricated on a glass or plastic substrate 1 coated with a transparent material such as indium-tin-oxide ("ITO") to form an anode 2. Such coated substrates are commercially available. The ITO-coated substrate is covered with at least a thin film of an electroluminescent organic material 3 and a final cathode layer 4, which is typically a metal or alloy.

Some particularly attractive applications of such devices are as displays in battery-powered units such as portable computers and mobile phones. Therefore, to extend the battery life of such units, there is a particularly strong need to increase the efficiency of the light-emissive devices. One route to improving efficiency is by careful choice and design of the light-emissive material itself. Another is by

optimising the physical layout of the display. A third is by improving the conditions for charge injection into and charge recombination in the emissive layer.

To improve the conditions for charge injection into and charge recombination in the emissive layer it is known to include a charge transport layer of an organic material such as polystyrene sulphonic acid doped polyethylene dioxythiophene ("PEDOT-PSS") between one or both of the electrodes and the emissive layer. A suitably chosen charge transport layer can enhance charge injection into the emissive layer and resist reverse flow of charge carriers, which favours charge recombination. It is also known to form the electrodes from materials having work functions that aid the desired flow of charge carriers. For example, a low work function material such as calcium or lithium is preferred as the cathode. PCT/WO97/08919 discloses a cathode formed of a magnesium:lithium alloy.

According to one aspect of the present invention there is provided an opto-electrical device comprising: an anode electrode; a cathode electrode; and an opto-electrically active region located between the electrodes; the cathode electrode including a first layer comprising a material having a work function below 3.5 eV and a second layer, of a different composition from the first layer, comprising another material having a work function below 3.5 eV.

The first layer is suitably closer to the opto-electrically active region than the second layer. The first layer may be adjacent to the opto-electrically active region or there may be one or more other layers (preferably electrically conductive layers) between the first layer and the opto-electrically active region. The opto-electrically active region is suitably in the form of a layer, preferably a layer of an opto-electrically active material. The opto-electrically active region is suitably active to emit light or to generate an electrical field in response to incident light. The device is preferably an electroluminescent device.

The thickness of the first layer is suitably less than 50 Å, preferably less than 30 Å, more preferably less than 25 Å or 20 Å. The thickness of the first layer could be

less than 15 Å or 10 Å. The thickness of the first layer is preferably in the range from 5 Å to 20 Å, most preferably around 15 Å. The first layer is preferably thinner than the second layer.

The thickness of the second layer is suitably less than 1000 Å, and preferably less than 500 Å. The thickness of the second layer is suitably more than 100 Å, and preferably more than 150 Å or 200 Å. The thickness of the second layer is preferably in the range from 100 Å to 500 Å. The second first layer is preferably thicker than the first layer.

The said material having a work function below 3.5 eV of which the first layer is comprised ("the first low work function material") preferably has a higher work function than the said material having a work function below 3.5 eV of which the second layer is comprised ("the second low work function material"), or could alternatively have a lower work function than it. The first and/or second low work function materials are suitably metals. The first low work function material is preferably a metal selected from the following list: Li, Ba, Mg, Ca, Ce, Cs, Eu, Rb, K, Sm, Na, Sm, Sr, Tb or Yb; or an alloy of two or more of such metals; or a fluoride, carbide, oxide or nitride of one or more of such metals; or an alloy of one or more of such metals together with another metal such as Al, Zr, Si, Sb, Sn, Zn, Mn, Ti, Cu, Co, W, Pb, In or Ag. The second low work function material is preferably a metal selected from the following list: Li, Ba, Mg, Ca, Ce, Cs, Eu, Rb, K, Sm, Na, Sm, Sr, Tb or Yb; or an alloy of two or more of such metals; or a fluoride, carbide, oxide or nitride of one or more of such metals; or an alloy of one or more of such metals together with another metal such as Al, Zr, Si, Sb, Sn, Zn, Mn, Ti, Cu, Co, W, Pb, In or Ag. The first and second low work function materials are preferably different materials. In one preferred embodiment the first low work function material is calcium and the second low work function material is lithium.

The first low work function material suitably has a work function less than 3.4 eV, or less than 3.3 eV or less than 3.2 eV, or less than 3.2 eV or less than 3.1 eV or less than 3.0 eV. The second low work function material suitably has a work

function less than 3.4 eV, or less than 3.3 eV or less than 3.2 eV, or less than 3.2 eV or less than 3.1 eV or less than 3.0 eV.

The first low work function material preferably does not cause significant degradation of the material of the active region when the two are in contact. The second low work function material may be a material that is capable of causing degradation of the material of the active region when the two are in contact. The first low work function material may, when in contact with the material of the active region, form an intermediate state between those of the material of the active region and those of the second layer.

The cathode may include a third layer located on the opposite side of the first and second layers from the opto-electrically active region. The third layer suitably comprises a material ("higher work function material") having a higher work function than those of the first and second low work function materials. The work function of the higher work function material is preferably greater than 3.5 eV or more preferably greater than 4.0 eV. The higher work function material is suitably a metal. The higher work function material and/or the third layer itself preferably has an electrical conductivity greater than 10^5 $(\Omega.cm)^{-1}$. The higher work function material is preferably Al, Cu, Ag, Au or Pt; or an alloy of two or more of those metals; or an alloy of one or more of those metals together with another metal. The thickness of the third layer is preferably in the range from 1000 Å to 10000 Å, preferably in the range from 2000 Å to 6000 Å, and most preferably around 4000 Å.

Suitably more than 50%, more than 80%, more than 90% or more then 95% of the first layer consists of the first low work function material. Preferably the first layer substantially wholly comprises the first low work function material. Most preferably the first layer consists of the first low work function material together with any impurities. Suitably more than 50%, more than 80%, more than 90% or more then 95% of the second layer consists of the second low work function material. Preferably the second layer substantially wholly comprises the second low work

function material. Most preferably the second layer consists of the second low work function material together with any impurities. Suitably more than 50%, more than 80%, more than 90% or more then 95% of the third layer consists of the higher work function material. The third layer preferably substantially wholly comprises the higher work function material. Most preferably the third layer consists of the higher work function material together with any impurities.

The second layer is preferably adjacent to the first layer. The third layer is preferably adjacent to the second layer. Alternatively, the cathode may comprise further layers located between the first, second and/or third layers. The cathode is preferably inorganic, most preferably metallic.

One of the electrodes is preferably light-transmissive, and most preferably transparent. This is preferably the anode electrode, which could be formed of tin oxide (TO), indium-tin oxide (ITO) or gold.

The opto-electrically active region may be light-emissive or (suitably on the application of a suitable electric field across it) or may be light-sensitive (suitably generating an electric field in response to incident light). The opto-electrically active region suitably comprises a light-emissive material or a light-sensitive material. Such a light-emissive material is suitably an organic material and preferably a polymer material. The light-emissive material is preferably a semiconductive and/or conjugated polymer material. Alternatively the light-emissive material could be of other types, for example sublimed small molecule films or inorganic light-emissive material. The or each organic light-emissive material may comprise one or more individual organic materials, suitably polymers, preferably fully or partially conjugated polymers. Example materials include one or more of the following in any combination: poly(p-phenylenevinylene) ("PPV"), poly(2-methoxy-5(2'-ethyl)hexyloxyphenylene-vinylene) ("MEH-PPV"), one or more PPV-derivatives (e.g. di-alkoxy or di-alkyl derivatives), polyfluorenes and/or co-polymers incorporating polyfluorene segments, PPVs and related co-polymers, poly(2,7-(9,9-di-n-octylfluorene)-(1,4-

phenylene-((4-secbutylphenyl)imino)-1,4-phenylene)) ("TFB"), poly(2,7-(9,9-di-n-octylfluorene) - (1,4-phenylene-((4-methylphenyl)imino)-1,4-phenylene-((4 - methylphenyl)imino) - 1,4-phenylene)) ("PFM"), poly(2,7 - (9,9 - di-n-octylfluorene) - (1,4-phenylene-((4-methoxyphenyl)imino)-1,4-phenylene- ((4-methoxyphenyl)imino)-1,4-phenylene)) ("PFMO"), poly (2,7-(9,9-di-n-octylfluorene) ("F8") or (2,7-(9,9-di-n-octylfluorene)-3,6-Benzothiadiazole) ("F8BT"). Alternative materials include small molecule materials such as Alq3.

There may be one or more other layers in the device. There may be one or more charge transport layers (preferably of more or more organic materials) between the active region and one or other of the electrodes. The or each charge transport layer may suitably comprise one or more polymers such as polystyrene sulphonic acid doped polyethylene dioxythiophene ("PEDOT-PSS"), poly(2,7-(9,9-di-n-octylfluorene)-(1,4-phenylene-(4-imino(benzoic acid))-1,4-phenylene-(4-imino(benzoic acid))-1,4-phenylene)) ("BFA"), polyaniline and PPV.

According to a second aspect of the present invention there is provided a method for forming an opto-electrical device, the method comprising: depositing an anode electrode; depositing over the anode electrode a region of an opto-electrically active material; depositing over the region of opto-electrically active material a material having a work function below 3.5 eV to form a first cathode layer; and depositing over the first cathode layer another material having a work function below 3.5 eV to form a second cathode layer of a different composition from the first cathode layer.

The present invention will now be described by way of example with reference to the accompanying drawings, in which:

figure 2 is a cross-section of a light-emissive device; and

figures 3 to 4 show data on the performance of several light-emissive devices.

The illustrated thicknesses of the layers in figure 2 are not to scale.

The device of figure 2 comprises an anode electrode 10 and a cathode electrode 11. Located between the electrode layers is an active layer 12 of light-emissive material. A charge transport layer 13 of PEDOT:PSS is located between the anode electrode 10 and the light-emissive layer 12. The device is formed on a glass substrate 14.

The metallic cathode 11 comprises three layers. Next to the emissive layer 12 is a first layer 15, of calcium. Over that is a second layer 16, of lithium. Over that is a third layer 17, of aluminium. As will be described below, this structure has been found to provide a significant increase in device efficiency.

To form the device of figure 2 a transparent layer of ITO to form the anode electrode 10 may first be deposited on a sheet of glass 14. The glass sheet could be a sheet of sodalime or borosilicate glass of a thickness of, for instance, 1mm. The thickness of the ITO coating is suitably around 100 to 150nm and the ITO suitably has a sheet resistance of between 10 and 30 Ω/□. ITO-coated glass substrates of this type are commercially available. As an alternative to glass, the sheet 14 could be formed of perspex. As an alternative to ITO, gold or TO could be used as the anode.

Over the ITO anode is deposited a hole transport or injecting layer 13. The hole transport layer is formed from a solution containing PEDOT:PSS with a ratio of PEDOT to PSS of around 1 to 5.5. The thickness of the hole transport layer is suitably around 500 Å. The hole transport layer is spin-coated from solution and then baked at around 200°C for 1 hour in a nitrogen environment.

Then the electroluminescent layer 15 is deposited. In this example, the electroluminescent layer is formed of 20% TFB in 5BTF8. The term 5BTF8 refers to poly (2,7-(9,9-di-*n*-octylfluorene) ("F8") doped with 5% poly-(2,7-(9,9-di-*n*-octylfluorene)-3,6-benzothiadiazole) ("F8BT"). the term TFB refers to poly(2,7-(9,9-di-n-octylfluorene)-(1,4-phenylene-((4-secbutylphenyl)imino)-1,4-phenylene)). This mixture is coated over the hole transport layer by spin-coating typically to a

thickness of around 750 Å. Other materials such as PPV could be used for the emissive layer. The emissive layer could be formed by other routes such as blade or meniscus coating and could be deposited in precursor form if desired.

The cathode is then deposited. The three distinct layers of the cathode are deposited by successive thermal evaporation steps *in vacuo* at a base pressure of less than 10^{-8} mbar. Preferably the vacuum is not broken between the successive steps, to reduce the possibility of contamination of the interfaces between the layers. One alternative to thermal evaporation is sputtering, but this is less preferred for at least the deposition of the layer 15 adjacent to the emissive layer since it may cause damage to the emissive layer 12. In the first thermal evaporation step the layer 15 is deposited. The layer 15 is of calcium and has a thickness of approximately 5 to 25 Å, preferably around 15 Å. In the second thermal evaporation step the layer 16 is deposited. The layer 16 is of lithium and has a thickness of around 100 to 500 Å. In the third thermal evaporation step the layer 17 is deposited. The layer 17 is of aluminium and has a thickness of around 4000 Å.

Finally, contacts are attached to the layers 10 and 17 and, although the aluminium layer 16 may act to some extent as an encapsulant, the device is preferably sealed in epoxy resin for environmental protection.

In use, when a suitable voltage is applied between the anode and the cathode the light-emissive layer is stimulated to emit light. This passes to a viewer through the transparent anode and the glass cover sheet.

The applicant has found that a device of this type has significantly increased efficiency. Figures 3 to 4 show data for the performance of devices of a similar device to that of figure 2 (devices E to H) and two comparative device designs (devices A to D and devices J to P).

The common structures of the devices were as follows:

- Substrate: glass
- Anode: ITO
- Charge transport layer: 1:5.5 PEDOT:PSS; thickness 500 Å
- Emissive layer: 4:1 5BTF8:TFB; thickness 750 Å

The cathodes of the devices were as follows:

Devices A to D:

- calcium layer of thickness 500 Å adjacent to emissive layer; and
- capping layer of aluminium of thickness 4000 Å.

Devices E to H:

- lithium layer of thickness 500 Å adjacent to emissive layer; then
- calcium layer of thickness 1000 Å; and
- capping layer of aluminium of thickness 4000 Å.

Devices J to P:

- lithium layer of thickness 25 Å adjacent to emissive layer; and
- capping layer of aluminium of thickness 4000 Å.

Figure 3 shows the peak measured efficiencies of the devices in Lm/W and Cd/A. Figure 4 shows the drive voltages for the devices at brightnesses of 0.01, 100 and 1000 Cd/m^2. Figure 3 shows that the peak efficiency of devices E to H is markedly greater than those of the other devices. Figure 4 shows that devices E to H do not suffer any significant increase in drive voltage, and have significantly lower drive voltages than devices J to P.

It is believed that, when the layer 15 of the cathode that is adjacent to the emissive layer 12 is sufficiently thin that the properties of the overlying cathode layer 16 can influence charge injection from the cathode into the emissive layer, there is an opportunity to select materials for the layers 15 and 16 such that by a combination of their properties the performance of the device can be enhanced. Possible mechanisms for this enhancement are believed to include: (a) prevention by the layer 15 of adverse interactions between organic layer(s) of the device (e.g. layer 15) and the material of the layer 16, whilst retaining at least some of the injection

properties of the material of the layer 16; and (b) the formation by the layer 15 (e.g. with organic layer(s) such as layer 15) of intermediate states that aid electron injection from the layer 16. The layer 15 should be sufficiently thin to allow the effect to occur but sufficiently thick that it can be deposited reproducibly and uniformly (without excessive defects). To exploit possible mechanism (a) the layer 16 could be formed from a material that is more reactive than that of layer 15, but has a lower work function.

A device of the type described above may form a pixel of a multi-pixel display device.

The devices described above may be varied in many ways within the scope of the present invention. For example, the capping layer 17 could be omitted; the layers could be formed of different materials; additional layers could be present, in the cathode or elsewhere in the device; or one or more additional charge transport layers could be provided between the light-emissive layer and either or both of the electrodes to assist charge transport between the respective electrode and the light-emissive layer and/or to resist charge transport in the opposite direction. The emissive material could be of the class of sublimed molecular films, as described for example in "Organic Electroluminescent Diodes", C. W. Tang and S. A. VanSlyke, Appl. Phys. Lett. 51, 913-915 (1987). The locations of the electrodes could be reversed so that the cathode is located at the front of the display (closest to the viewer) and the anode is at the back.

The same principles may be applied to devices for the detection rather than the generation of light. By replacing (if necessary) the light-emissive material with a material that is capable of generating an electrical field in response to light the improved characteristics of the improved electrodes as described above may be used to enhance detection voltages and/or efficiency.

The applicant draws attention to the fact that the present invention may include any inventive feature or combination of features disclosed herein either implicitly or

explicitly or any generalisation thereof, without limitation to the scope of any of the present claims. In view of the foregoing description it will be evident to a person skilled in the art that various modifications may be made within the scope of the invention.

CLAIMS

1. An opto-electrical device comprising:

an anode electrode;

a cathode electrode; and

an opto-electrically active region located between the electrodes;

the cathode electrode including a first layer comprising a material having a work function below 3.5 eV and a second layer, of a different composition from the first layer, comprising another material having a work function below 3.5 eV.

2. An opto-electrical device as claimed in claim 1, wherein the first layer is closer to the opto-electrically active region than the second layer.

3. An opto-electrical device as claimed in claim 2, wherein the thickness of the first layer is less than 25 Å.

4. An opto-electrical device as claimed in claim 2 or 3, wherein the second layer is thicker than the first layer.

5. An opto-electrical device as claimed in any of claims 2 to 4, wherein the thickness of the second layer is greater than 100 Å.

6. An opto-electrical device as claimed in any of claims 2 to 5, wherein the said material having a work function below 3.5 eV of which the first layer is comprised has a higher work function than the said material having a work function below 3.5 eV of which the second layer is comprised.

7. An opto-electrical device as claimed in any preceding claim, wherein the said material having a work function below 3.5 eV of which the first layer is comprised is a metal.

8. An opto-electrical device as claimed in claim 7, wherein the said material having a work function below 3.5 eV of which the first layer is comprised is Li, Ba, Mg, Ca, Ce, Cs, Eu, Rb, K, Sm, Na, Sm, Sr, Tb or Yb.

9. An opto-electrical device as claimed in any preceding claim, wherein the said material having a work function below 3.5 eV of which the second layer is comprised is a metal.

10. An opto-electrical device as claimed in claim 9, wherein the said material having a work function below 3.5 eV of which the second layer is comprised is Li, Ba, Mg, Ca, Ce, Cs, Eu, Rb, K, Sm, Na, Sm, Sr, Tb or Yb.

11. An opto-electrical device as claimed in any preceding claim, wherein the cathode includes a third layer located on the opposite side of the first and second layers from the opto-electrically active region, the third layer comprising a material having a work function greater than 3.5 eV..

12. An opto-electrical device as claimed in claim 11, wherein the thickness of the third layer is greater than 1000 Å.

13. An opto-electrical device as claimed in claim 11 or 12, wherein the said material having a work function above 3.5eV has an electrical conductivity greater than 10^5 $(\Omega.cm)^{-1}$.

14. An opto-electrical device as claimed in any of claims 11 to 13, wherein the said material having a work function above 3.5eV is aluminium.

15. An opto-electrical device as claimed in any preceding claim, wherein the opto-electrically active region is light-emissive.

16. An opto-electrical device as claimed in any preceding claim, wherein the opto-electrically active region comprises a light-emissive organic material.

17. An opto-electrical device as claimed in claim 16, wherein the light-emissive organic material is a polymer material.

18. An opto-electrical device as claimed in claim 17, wherein the light-emissive organic material is a conjugated polymer material.

19. An opto-electrical device as claimed in any of claims 16 to 18, comprising a charge transport layer between the light-emissive organic material and one of the electrodes.

20. A method for forming an opto-electrical device, the method comprising:

depositing an anode electrode;

depositing over the anode electrode a region of an opto-electrically active material;

depositing over the region of opto-electrically active material a material having a work function below 3.5 eV to form a first cathode layer; and

depositing over the first cathode layer another material having a work function below 3.5 eV to form a second cathode layer of a different composition from the first cathode layer.

21. An opto-electrical device substantially as herein described with reference to figures 2 to 4 of the accompanying drawings.

22. A method for forming an opto-electrical device substantially as herein described with reference to figures 2 to 4 of the accompanying drawings.

ABSTRACT

OPTO-ELECTRICAL DEVICES

An opto-electrical device comprising: an anode electrode; a cathode electrode; and an opto-electrically active region located between the electrodes; the cathode including a first layer comprising a material having a work function below 3.5 eV and a second layer, of a different composition from the first layer, comprising another material having a work function below 3.5 eV.

Figure 2

Fig. 1

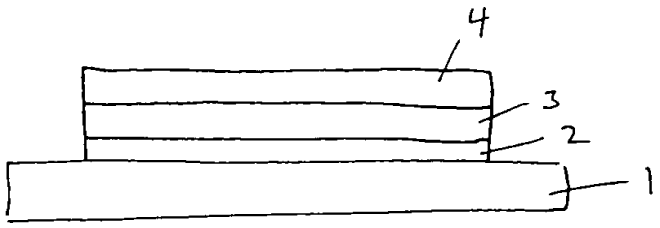

Fig. 2

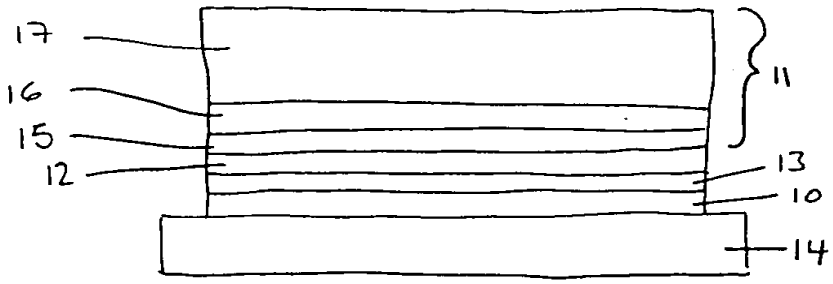

Fig.3

Different cathode layer structure with Li/Ca/Al
PEDOT=Ba/PEDT/6:Sp/PSS/1 (1:5.5 PEDT:PSS) 500Å
Emitter = R/5BTF8/1:R/TFB/1 (4:1) 750Å

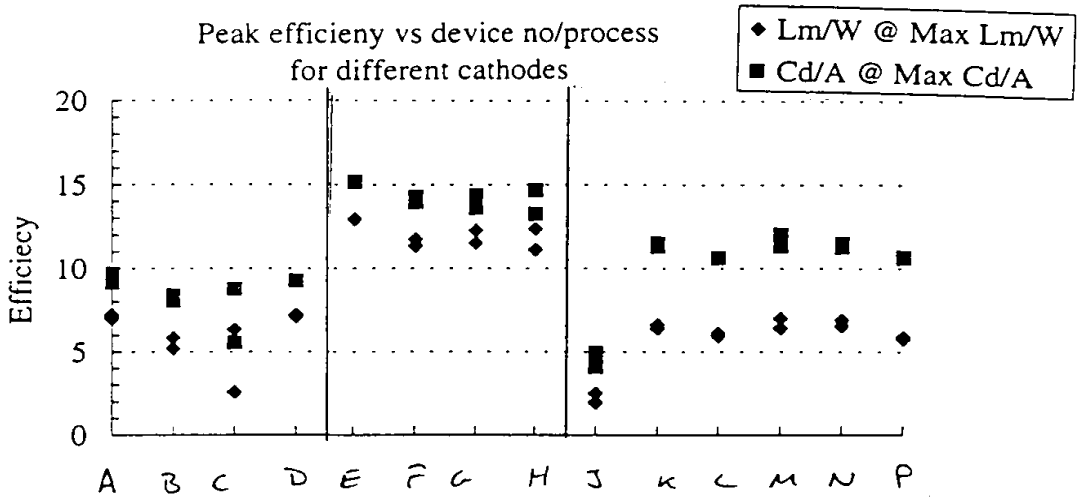

Fig.4